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Developments in Bleaching Technology
Focus on Reducing Capital, Operating Costs

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Developments in Bleaching Technology Focus on Reducing Capital, Operating Costs

By Thomas Dyer and Art J. Ragauskas

In 1867, Benjamin Disraeli delivered his famous speech in Edinburgh, Scotland, where he stated that "Change is inevitable in a progressive country. Change is constant." A brief review of research efforts underway in pulping and bleaching would certainly insure this statement is as relevant today as it was 135 years ago.

A review of scientific literature on pulping and bleaching research a decade ago illustrates that efforts in the early 1990s were dominated by environmental issues. The major thrust of research was to reduce the impact of pulping and bleaching operations on the environment. A primary focus of much of that work was on reducing or eliminating the use of chlorine in order to reduce the formation of chlorinated by-products in mill pulping and bleaching operations, and subsequently, discharged in mill effluent. Since that time, the shift to widespread use of modern elemental chlorine free (ECF) and, to a lesser extent, total chlorine free (TCF) pulping and bleaching sequences has been a fundamental change in mill operations around the world.

CAPITAL/ OPERATING COSTS REDUCTION OPTIONS.

The research landscape has dramatically changed over the past few years. Research and development efforts are now focused primarily on improving the capital and operating performance of modern ECF and TCF operations, while at the same time addressing society's needs for environmental performance. In North America, and to some extent in other areas, this focus is magnified by the severe constraints imposed on capital investment by the industry's poor financial performance. Chemical pulp capacity in North America is stagnant, or even declining. In turn, this has shifted the focus of investments and research to improving the operating costs of existing production lines with minimal capital investment.

This article provides a brief review of short- and long-term research activities addressing reduced pulp bleaching capital costs and operating costs. These activities cover a broad span of competing technologies, including the following four major areas:

- Short sequence bleaching technologies
- Optimization of bleaching chemicals
- Bleaching catalysts for peroxide and oxygen delignification
- Low lignin content trees

SHORT SEQUENCE OPTIONS.

An attractive means of reducing the capital costs of modern ECF/TCF bleach plants is the elimination of entire bleaching stages and/or bleach plant washers to produce a short sequence process. Short-sequence bleaching is defined as a bleaching sequence which produces an 88% ISO brightness pulp in four stages or less for softwood kraft (SW) pulp, and in three stages or less for hardwood (HW) kraft or sulfite pulps.¹

Rapson,² Histed,³ and Liebergott⁴ were among some of the earliest proponents of simplifying kraft bleach plant operations as a way to reduce kraft bleach plant capital costs. However, for pulp mills using ECF/TCF processes, the use of a short bleaching sequence to produce high brightness pulp, while maintaining low chemical costs, presents a significant challenge. Chandrasekaran⁵ reported that laboratory and mill-based studies examining the use of a D(E+O+P)D sequence indicated that this process yielded fully bleached HW and SW pulps with final brightness values of 90.4%, and 88.7%, respectively. However, an increase in chemical costs was noted as well.

Recently, McDonough, Courchene, and Baromès⁶ have explored the use of a rapid D₀ stage (i.e., D^R) to bleach HW and SW kraft pulps. The D^R stage utilizes a high-shear mixer and a small retention tube, employs a moderate kappa factor, and has operating temperatures of 50 to 70°C. This technology provides a low-capital cost approach for retrofitting an ECF bleach plant line to achieve pulp brightness and/or to meet environmental requirements.

At the recent 2001 TAPPI Pulping Conference, G. Goyal presented a seminar titled "Efforts to Reduce Chlorine Dioxide Consumption for Chip and Sawdust Line." The planned application of a D^R-stage at Potlatch Corp.'s Lewiston, Idaho, kraft pulp mill was reviewed. This technology is being applied as a low-capital cost approach to minimize chlorine dioxide bleaching costs while maximizing pulp brightness.

OPTIMIZATION: HYDROGEN PEROXIDE REINFORCEMENT.

The use of various combinations of alternative bleaching chemicals is another approach that provides options to reduce capital and operating costs. A variety of bleaching chemicals has been examined as a means of supplementing chlorine dioxide in ECF kraft bleaching operations. However, the use of hydrogen peroxide remains one of the most practical, low capital cost means of improving ECF bleaching operations.

An extensive laboratory/pilot study by Henrique⁷ examined several peroxide reinforced bleaching sequences for eucalyptus pulps, including D(E+O)DD, D(E+O+P)DD, D(E+O)DP, D(E+O)DP(QP), and D(E+O+P)DP. The well-established bleaching benefits of peroxide were shown, as a substitution factor of 1.8 kg ClO₂/kg H₂O₂ when changing the D₂ stage for P was demonstrated. The use of peroxide in the initial extraction stage was also found beneficial, but its use here yielded a lower substitution factor. The authors concluded that the use of peroxide provides a simplistic means of

increasing production, without having to invest in additional chlorine dioxide capacity, while maintaining pulp quality.

It has also now been well documented that the bleaching/delignification capabilities of hydrogen peroxide can be extended with the use of high temperature/high pressure operating conditions. From a chemistry perspective, these results are indicative of a chemical process that could be improved with the use of specialized catalysts.

In fact, a review by Suchy and Argyropoulos⁸ highlighted recent developments in the use of catalyst and activation technologies for hydrogen peroxide and oxygen pulp bleaching. Although the developments in this field have been rapid, routine applications of these technologies in a modern pulp mill are several years away and will require additional research.

OPTIMIZATION: OZONE APPLICATIONS

Any discussion of notable low-capital bleaching developments would certainly include the use of low-consistency D/Z and Z/D bleaching stages. A recent technical report by Sundar⁹ highlights the benefits of approaches using ozone. The laboratory results documented the well-known synergistic bleaching interactions encountered when ozone and chlorine dioxide are applied in a single stage.

The authors also reviewed the economic benefits of retrofitting a low consistency C/D, D/C, or D100 stage with a Z/D or D/Z stage. Further, it demonstrated that this approach can provide a minimal capital cost approach for mills looking for alternatives to chlorine bleaching or for those looking to increase capacity.

CATALYSTS AND BIOTECHNOLOGY

The use of xylanase as a pretreatment to ECF/TCF kraft pulp bleaching operations has become a readily available low-capital improvement tool for pulp bleaching operations. As reported by Tolan and Thibault,¹⁰ at least 11 mills in North America have used this biotechnology approach to improve pulp-bleaching operations as of 1999. Additional mill applications have been documented in European and South American pulp mills for ECF/TCF applications.

The benefits of a xylanase pretreatment can be readily captured by the addition of the enzyme to the brownstock high-density storage chest. The xylanase pretreatment has been shown to reduce the amounts of bleaching chemical needed in subsequent bleaching operations. In general, hardwood kraft pulps respond more favorable to a xylanase pretreatment than softwood kraft pulps. Typically, in ECF pulp mills, xylanase is applied to reduce ClO_2 usage in either the D_0 or D_1 stage. Alternatively, for a given level of chlorine dioxide applied, the introduction of a xylanase stage can yield higher final

brightness values. This latter xylanase application is of practical interest for many TCF pulp mill situations.

OXYGEN DELIGNIFICATION

Looking further into the future, genetic research is actively being pursued on a global basis as a means of developing wood resources that will provide many benefits to pulp manufacturers. These include the development of new wood resources that will be readily pulpable at low temperatures and ones that will only require one or two bleaching stages.¹¹

Until this future arrives, research efforts at the Institute of Paper Science and Technology (IPST) are focused on developing new technological solutions for improving the overall performance of oxygen delignification systems. This project is a collaborative Department of Energy (DOE) funded research project involving Dr. H. Jameel, at North Carolina State University, and Drs. Lucia and Ragauskas at IPST.

This research is focused on identifying the optimal kraft digester operating conditions that will yield a pulp with enhanced lignin reactivity. Enhanced reactivity can benefit or improve oxygen delignification in modern single and double-stage oxygen reactors. Research has already demonstrated that this approach can provide improved strength and yield benefits after a single or double O-stage.

Mini-oxygen stage. An alternative technology is to use a mini-oxygen (mini-O) stage prior to an O or D₀-stage as a low-capital cost alternative to bleaching kraft pulps. This is not a new technology, as has been previously reported. In 1994, McKenzie¹² reported on the benefits of introducing a pretention tube on a washing retention tube, converting it to an (E+O) stage prior to DED at the mill. Incorporating a mini-O stage allowed the mill to cook to a standard permanganate number, and then reduce the amount of lignin in the DE pulp, thereby facilitating a low AOX bleach sequence (i.e., DE(E+O)DED). The mini-O stage consists of an upflow tube, with approximately 30 min. of retention time, 80 to 90 psig oxygen pressure, 1% NaOH, and 70 to 80°C.

The mini-O stage was also shown to delignify the pulp by approximately 25% prior to a conventional oxygen stage. A subsequent report by Histed¹³ examined the use of an enhanced "poor man's O," which involved a 0.05 kappa factor D pretreatment followed by a higher than normal temperature (E+O) stage. Depending upon the exact charge of caustic used and the operating conditions, 40% to 50% delignification was achieved on a SW kraft furnish. The overall bleach sequence was D_{kf:0.05}(E+O)D₀(E+P)(DED), with a 2-minute retention time in the initial low-kappa factor D-stage. There is also no washing between the retention tubes and the final D-stage. This simplified bleaching approach was shown to provide a low-capital cost alternative to an O-stage, while reducing chemical costs and maintaining pulp properties.

Reported in 2000, research studies by Chakar¹⁴ explored the potential to delignify high and low-kappa kraft pulps via a mini-O stage and examined the use of (E+O)(E+O) vs (E+O)D_{0.05kf}(E+O) sequences. The addition of a low charge of chlorine dioxide was shown to increase the extent the pulp was delignified by 43% for low lignin content pulps, with minimal damage to pulp viscosity. From a fundamental lignin chemistry perspective, the mini-O stage takes full advantage of our current understanding of residual lignin chemistry.

Numerous studies indicate that most kraft pulps contain a fraction of reactive lignin and intragraft lignin. This latter fraction has been a subject of extensive studies and certainly is due in part to condensed phenolics, p-hydroxyl phenolics, and etherified units in the pulp. For this reason, the preferred approach is to remove the readily reactive lignin in a kraft pulp with the most efficient and low capital cost bleaching equipment available.

Enhanced mini-O. Dyer¹⁵ further examined the benefits of an enhanced poor man's oxygen stage and demonstrated that a (E+O)D_{0.05}(E+O) sequence was more effective at delignification than either D_{kf:0.05}(E+O)(E+O), (E+O)(E+O) or a simple (E+O) stage. The authors attributed this enhanced delignification to removal by the initial mini-O stage of easily oxidized lignin prior to the low kappa factor charge of chlorine dioxide.

This work did not evaluate the effects of black liquor carryover, but a subsequent study examined these issues.¹⁶ Laboratory studies have shown that carryover does decrease the overall efficiency of the (E+O)D_{0.05}(E+O) approach, but that significant lignin removal was still accomplished.

Research studies also evaluated the effect of reinforcing the mini-O stages with small charges of hydrogen peroxide. The addition of hydrogen peroxide in the last stage of a {(E+O)* D_{kf:0.05}(E+O)*} sequence was shown to have had a greater impact on bleaching performance than if placed in the front of the sequence. The * indicates with or without peroxide, while the brackets indicate there is no washing between stages.

Although further studies are needed to validate the application of mini-O technologies for modern ECF operations, studies to-date and recent accomplishments suggest the development of new low capital bleaching alternatives will be available shortly.

In closing, it is perhaps best to reflect on Darwin's law of evolution: "It is not the strongest of the species that survive, nor the most intelligent, but the one most responsive to change."

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